

1430020

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(54) TREATMENT OF METAL SURFACES

(71) We, PYRENE CHEMICAL SERVICES LIMITED, a British Company of Ridgeway, Iver, Buckinghamshire, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

To provide improved appearance, longer life and increased reliability for metal-based consumer and industrial products, it has become accepted practice to conversion coat metallic surfaces before application of a paint, lacquer or oil.

In forming conversion coatings on metallic surfaces, various treatment steps may be employed such as described in (1) Metal Handbook, Volume 2, 8th Edition, pp. 529—547, American Society for Metals and (2) J. I. Maurer, "Preparation of Metal Surface for Organic Finishes"—American Society of Tool and Manufacturing Engineers, Paper FC 68—652. The steps that are normally employed are (1) cleaning, (2) water rinsing, (3) forming a conversion coating by contacting the surface with a suitable coating composition and (4) water rinsing.

Conversion coated metallic surfaces may be given a post-treatment to impart further humidity and corrosion resistance. The post-treatment or final rinse frequently is a chromium-containing composition such as described in U.S. Patents Nos. 3,222,226 and 2,970,935.

In preparing metal to receive paint, it is widely understood that application of a dilute chromium-containing solution to the conversion coating improves that coating as a base for paint both with respect to corrosion resistance and humidity resistance of the painted surface. Depending on the method of painting, the post-treated conversion coating may be dried or the non-reacted post-treatment solution removed by rinsing with deionised water and the work then dried. In the case of electrodeposited paint, drying may not be necessary.

Despite the above discussion concerning post-treatment, chromium-containing post-treatment compositions are not ideal. Thus, the use of heavy metals such as chromium in metal treating lines may result in pollution. Furthermore, many chromium-containing compositions also have the side effect of leading to blistering of a final organic film e.g. paint under conditions of high humidity at areas where the post-treatment solution can concentrate before drying. One method of overcoming this problem is to rinse the work with water, preferably deionised water as mentioned above, before painting. This is especially desirable before electropainting where the paints are water based and soluble contaminants can unbalance the paint. Many chromium-containing post-treatments however wash off in this water rinse thus losing their ability to inhibit paint loss due to under paint corrosion.

We have now found that it is advantageous for metal surfaces having certain conversion coatings to be given a post-treatment with a composition containing a tannin. According to the invention, a method for coating a metal surface comprises coating the surface with a conversion coating composition containing iron or zinc and phosphate ions and subsequently contacting the thus-coated surface with a tannin-containing composition. We have found that by means of the method surfaces can be obtained which minimise or eliminate the tendency for blisters to form in a subsequently applied organic-based film e.g. a decorative organic coating under conditions of high humidity when water condenses on the film.

The invention is of particular value with surfaces of steel e.g. cold rolled, ground, pickled and hot rolled steel, galvanised steel and aluminium, i.e. metallic surfaces containing zinc, iron or aluminium. In the past the blistering problem has been particularly serious with galvanised surfaces. The post-treatment involved in the method according to the invention does not detract from the ability of the treated surfaces to allow satis-

factory adhesion of an organic coating. Furthermore, the disadvantages of post-treatments using chromium-containing compositions can be avoided.

5 The use of tannins or tannic acid as a treatment for bare or corroded metallic surfaces has been disclosed in U.S. Patents Nos. 1,798,218; 2,460,453; 2,460,454; 2,460,455; 2,460,456; 2,460,457; 2,460,458; 2,460,459; 2,460,460; 2,460,461; 2,460,462; 2,460,463; 2,460,464; 2,460,465; 2,460,466; 2,460,467; 2,460,468; 2,460,469; 2,460,470; 2,460,471; 2,460,472; 2,460,473; 2,460,474; 2,460,475; 2,460,476; 2,460,477; 2,460,478; 2,460,479; 2,460,480; 2,460,481; 2,460,482; 2,460,483; 2,460,484; 2,460,485; 2,460,486; 2,460,487; 2,460,488; 2,460,489; 2,460,490; 2,460,491; 2,460,492; 2,460,493; 2,460,494; 2,460,495; 2,460,496; 2,460,497; 2,460,498; 2,460,499; 2,460,500; 2,460,501; 2,460,502; 2,460,503; 2,460,504; 2,460,505; 2,460,506; 2,460,507; 2,460,508; 2,460,509; 2,460,510; 2,460,511; 2,460,512; 2,460,513; 2,460,514; 2,460,515; 2,460,516; 2,460,517; 2,460,518; 2,460,519; 2,460,520; 2,460,521; 2,460,522; 2,460,523; 2,460,524; 2,460,525; 2,460,526; 2,460,527; 2,460,528; 2,460,529; 2,460,530; 2,460,531; 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2,460,623; 2,460,624; 2,460,625; 2,460,626; 2,460,627; 2,460,628; 2,460,629; 2,460,630; 2,460,631; 2,460,632; 2,460,633; 2,460,634; 2,460,635; 2,460,636; 2,460,637; 2,460,638; 2,460,639; 2,460,640; 2,460,641; 2,460,642; 2,460,643; 2,460,644; 2,460,645; 2,460,646; 2,460,647; 2,460,648; 2,460,649; 2,460,650; 2,460,651; 2,460,652; 2,460,653; 2,460,654; 2,460,655; 2,460,656; 2,460,657; 2,460,658; 2,460,659; 2,460,660; 2,460,661; 2,460,662; 2,460,663; 2,460,664; 2,460,665; 2,460,666; 2,460,667; 2,460,668; 2,460,669; 2,460,670; 2,460,671; 2,460,672; 2,460,673; 2,460,674; 2,460,675; 2,460,676; 2,460,677; 2,460,678; 2,460,679; 2,460,680; 2,460,681; 2,460,682; 2,460,683; 2,460,684; 2,460,685; 2,460,686; 2,460,687; 2,460,688; 2,460,689; 2,460,690; 2,460,691; 2,460,692; 2,460,693; 2,460,694; 2,460,695; 2,460,696; 2,460,697; 2,460,698; 2,460,699; 2,460,700; 2,460,701; 2,460,702; 2,460,703; 2,460,704; 2,460,705; 2,460,706; 2,460,707; 2,460,708; 2,460,709; 2,460,710; 2,460,711; 2,460,712; 2,460,713; 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2,460,805; 2,460,806; 2,460,807; 2,460,808; 2,460,809; 2,460,810; 2,460,811; 2,460,812; 2,460,813; 2,460,814; 2,460,815; 2,460,816; 2,460,817; 2,460,818; 2,460,819; 2,460,820; 2,460,821; 2,460,822; 2,460,823; 2,460,824; 2,460,825; 2,460,826; 2,460,827; 2,460,828; 2,460,829; 2,460,830; 2,460,831; 2,460,832; 2,460,833; 2,460,834; 2,460,835; 2,460,836; 2,460,837; 2,460,838; 2,460,839; 2,460,840; 2,460,841; 2,460,842; 2,460,843; 2,460,844; 2,460,845; 2,460,846; 2,460,847; 2,460,848; 2,460,849; 2,460,850; 2,460,851; 2,460,852; 2,460,853; 2,460,854; 2,460,855; 2,460,856; 2,460,857; 2,460,858; 2,460,859; 2,460,860; 2,460,861; 2,460,862; 2,460,863; 2,460,864; 2,460,865; 2,460,866; 2,460,867; 2,460,868; 2,460,869; 2,460,870; 2,460,871; 2,460,872; 2,460,873; 2,460,874; 2,460,875; 2,460,876; 2,460,877; 2,460,878; 2,460,879; 2,460,880; 2,460,881; 2,460,882; 2,460,883; 2,460,884; 2,460,885; 2,460,886; 2,460,887; 2,460,888; 2,460,889; 2,460,890; 2,460,891; 2,460,892; 2,460,893; 2,460,894; 2,460,895; 2,460,896; 2,460,897; 2,460,898; 2,460,899; 2,460,900; 2,460,901; 2,460,902; 2,460,903; 2,460,904; 2,460,905; 2,460,906; 2,460,907; 2,460,908; 2,460,909; 2,460,910; 2,460,911; 2,460,912; 2,460,913; 2,460,914; 2,460,915; 2,460,916; 2,460,917; 2,460,918; 2,460,919; 2,460,920; 2,460,921; 2,460,922; 2,460,923; 2,460,924; 2,460,925; 2,460,926; 2,460,927; 2,460,928; 2,460,929; 2,460,930; 2,460,931; 2,460,932; 2,460,933; 2,460,934; 2,460,935; 2,460,936; 2,460,937; 2,460,938; 2,460,939; 2,460,940; 2,460,941; 2,460,942; 2,460,943; 2,460,944; 2,460,945; 2,460,946; 2,460,947; 2,460,948; 2,460,949; 2,460,950; 2,460,951; 2,460,952; 2,460,953; 2,460,954; 2,460,955; 2,460,956; 2,460,957; 2,460,958; 2,460,959; 2,460,960; 2,460,961; 2,460,962; 2,460,963; 2,460,964; 2,460,965; 2,460,966; 2,460,967; 2,460,968; 2,460,969; 2,460,970; 2,460,971; 2,460,972; 2,460,973; 2,460,974; 2,460,975; 2,460,976; 2,460,977; 2,460,978; 2,460,979; 2,460,980; 2,460,981; 2,460,982; 2,460,983; 2,460,984; 2,460,985; 2,460,986; 2,460,987; 2,460,988; 2,460,989; 2,460,990; 2,460,991; 2,460,992; 2,460,993; 2,460,994; 2,460,995; 2,460,996; 2,460,997; 2,460,998; 2,460,999; 2,460,1000.

10 In the method according to the invention the phosphate-containing composition is a composition known for the formation of conversion coatings.

15 Examples of such compositions are described in U.S. Patents Nos. 2,835,617 and 2,609,308.

20 The tannins used in accordance with the invention are substances having the chemical structure of natural tannins and may be vegetable tannins i.e. polyphenolic compositions extracted from various plants including trees.

25 Natural tannin extracts have been described in U.S. Patent No. 2,854,368.

30 Natural tannin extracts can be classified according to their chemical properties as: (a) hydrolysable tannins; (b) condensed tannins; and (c) mixed tannins containing both hydrolysable and condensed tannins.

35 Hydrolysable tannins yield water soluble products upon hydrolysis with boiling dilute mineral acids whereas under these conditions complex tannin extracts form precipitates known as "tanners red" or phlobaphene. This classification somewhat corresponds to the "catechol tannins" (condensed) and "pyrogallol tannins" (hydrolysable). Examples of suitable vegetable tannins are extracts of Chinese gall (tannic acid), myrobalan, chestnut wood, divi-divi, valonia, sumac, chinchona, mangrove, wattle, eucalyptus, cutch, quebracho, hemlock, mimosa, oak and gambier.

45 Preferred extracts are tannic acid (National Formulary) and, particularly, quebracho extract. These are of particular value as they not only are useful against the blister formation already mentioned but also have a significant corrosion resistance effect on the painted treated surfaces.

50 Tannin extracts are also available as sulphited compositions in which the extract is treated with a sulphiting composition to improve the water solubility of the extract. The non-sulphite containing compositions are however preferred in accordance with the invention.

55 It has also been found that when the tannin extracts are subjected to NMR (nuclear magnetic resonance) analysis, the preferred tannins have a molar aromatic/alkyl ratio greater than 2, preferably 2 to 5. By "alkyl" is meant the portion of the molecule consisting of satur-

ated aliphatic groups. These groups are detected by NMR analysis as the protons (or hydrogen atoms) from $-\text{CH}$ or $-\text{CH}_2$ portions of the sucrose fragments of the tannins. By "aromatic" is meant the portion of the molecule consisting of aryl groups. These are detected by NMR analysis as the protons attached to carbon atoms in benzene rings in the polyphenolic portion of the tannin.

60 The amount of tannin containing composition (based on natural tannin extract) used in the post-treatment step may be less than 1% by weight of the total bath composition, preferably 0.1 to 10 g/l, and even more preferably 0.25 to 2 g/l.

65 The bath temperature for the tannin-containing composition may range from ambient to 200°F. The pH of the bath for the tannin-containing composition may range from 3 to 8, preferably 4.0 to 6.0.

70 A desirable tannin concentrate composition which can be used to formulate the bath for the post-treatment of conversion coatings is aqueous and contains 5 to 60% by weight, preferably 15 to 35% by weight tannin (based on tannin extract). It has been found that this concentrate may be directly added to the bath composition without significant time delays. The difficulty with such a composition is that the tannin tends to precipitate out during shipment. This can be avoided by adjusting the pH of the composition with, for example, NaOH to an alkaline pH, preferably 7.5 to 10, more preferably about 8.

75 Other ingredients which may be added to the tannin concentrate composition include aluminium fluoride. It is desirable that any additional ingredients do not tend to increase the precipitation of the tannin, as does phosphoric acid, and/or do not inhibit the desirable corrosion and humidity resistance properties produced by the use of the final compositions. For use in the method of the present invention such a concentrate is diluted and its pH adjusted as necessary, generally with phosphoric acid.

80 The following Examples illustrate the invention.

EXAMPLE 1

85 A solution was prepared in a five gallon laboratory spray tank which consisted of a solution of a 1/2 ounce per gallon of a commercial surface cleaner and heated to 150°F. A second solution was prepared which consisted of a zinc phosphating composition containing 1.5 g/l zinc ions, 6.4 g/l phosphate ions, 0.11 g/l nitrite ion, 0.5 g/l nickel ions and 0.4 g/l fluoride ions and heated to 150°F. Four by twelve inch minimum spangle commercial hot dip galvanized (GALV.) steel panels, temper rolled and four by twelve inch SAE 1010, cold rolled mild steel (CRS) panels were sprayed in the sequence one minute in the cleaner, one-half minute fresh warm water

rinse in an auxiliary spray tank, one minute in the phosphating bath, one minute in cold water spray rinse, and finally one-half minute in a five gallon spray tank wherein was mixed the post-treatment composition of the present invention by dissolving nineteen grams of the tannin extract in the five gallons (=22.73 litres) of water in the tank and adjusting the pH of the solution to 4.5 with reagent grade hydrofluoric acid. Following this treatment, the panels were dried in a circulating oven for five minutes at 275°F, and air cooled. Control panels were prepared by the same sequence except that they were oven dried after the rinse following the zinc phosphating step, or alternatively post-treated by immersion in a commercial post-treatment consisting of 0.04% chromic acid at a pH of 4, and oven dried.

These panels were then painted with an automotive body paint system consisting of an

epoxy primer, an epoxy guide coat, and two coats of an enamel top coat to a total film build of 2½ to 3 thou.

They were then subjected to either the standard ASTM B117-61 salt spray test or the ASTM Standard 2247-64T humidity test. Results are tabulated along with the tannin extract used for the test according to the standard system. Therein humidity blisters are rated VF for very few, F for few, FM for few to medium, M for medium, D for dense, and from 9 for very small to 1 for very large; 10 indicates no blistering. Salt spray panels are rated in terms of the amount of loss of paint from a scribe in 1/16 inch increments. Thus 0 means less than 1/16, and 0-2 means essentially no creepage (hence the 0) except in one or two spots (hence the s) for a distance of 2/16 inch (hence the 2). N indicates no loss of paint. These results are tabulated in Table I.

TABLE I

	Rinse	Metal	336 Hours Salt Spray	336 Hours Humidity
45	Control—Commercial Chrome Rinse	CRS	0—1	VF8
	"	Galv.	2—5	D-9
50	Control—Deionized Water	CRS	3—4	10
	"	Galv.	7—9	D-8
	Control—Tap Water	CRS	3—4	10
	"	Galv.	7—9	D-6
	Tannic Acid (NF-Fluffy Grade from Merck)	CRS	0—1	10
55	"	Galv.	N	10
	Quebracho Extract (Non Sulfite-Trask)	CRS	1—3	10
	"	Galv.	N	10

These results show that with many tannin materials corrosion resistance as represented by salt spray resistance are better than with a tap water final rinse and approaches the results obtained with conventional dilute chromium containing post-treatments. The humidity results are consistently better than standard post-treatments.

EXAMPLE 2

SAE 1010 cold rolled steel panels were coated as described in Example 1. The post-treatments employed were 1 g/l quebracho adjusted to a pH of 4.5 with phosphoric acid and a trivalent chromium post-treatment containing .02% by weight trivalent chromium and .004% by weight hexavalent chromium at

a pH of 4.3 as described in U.S. 3,279,958. This chrome containing post-treatment may be used with electrodeposited paints because it can be rinsed with deionized water (DIW) to remove soluble materials from the conversion coated work without harming corrosion and humidity resistance after painting, thus avoiding the contamination of the water based paint. Further panels were merely tap water rinsed after the conversion coating step. One set was air dried and the other oven dried at 275°F. for 5 minutes. These panels were electropainted with two commercial electroprimers—Forbes ED 1124 and Forbes ED 2000; and exposed to the ASTM B117-61 as described above for two weeks. The results are shown in Table 2.

TABLE 2

	Rinse	Drying	Paint	336 Hours Salt Spray
5	Control—Commercial Chrome	Air	ED 2000	1—2
	" " "	Oven	ED 2000	1—1
	Quebracho Extract	Air	ED 2000	1—1
	" " "	Oven	ED 2000	0—1
	Control—DIW	Air	ED 2000	3—4
	" " "	Oven	ED 2000	0—1
10	Control—Commercial Chrome	Air	ED 1124	1—3
	" " "	Oven	ED 1124	0—1
	Quebracho Extract	Air	ED 1124	0—1
	" " "	Oven	ED 1124	0—1
15	Control—DIW	Air	ED 1124	1—4
	" " "	Oven	ED 1124	1—4

These results show that the tannin containing post-treatments have the further advantage that they do not lose their ability when the post treatment is deionized water rinsed in order to remove all soluble materials capable of contaminating further processing such as electrophoretic paints which are water based paint materials.

cold rolled steel panels were conversion coated as in Example 1.

They were post-treated with a quebracho extract solution and adjusted with phosphoric acid to a pH of 4.5 applied by spray with the concentration varied from 1/4 g/l to 1 g/l. Controls post-treated with the same commercial chromium-containing post-treatment described in Example 1 were also prepared. All panels were oven dried 5 minutes at 275°F. and painted with the automotive body paint system described in Example 1. The results of the salt spray and humidity tests are given in Table 3.

EXAMPLE 3

Minimum spangle temper rolled commercial hot dip galvanized steel panels and SAE 1010

TABLE 3

	Rinse	CRS		GALV.	
		Salt	Humidity	Salt	Humidity
45	Control—Commercial Chrome	0—1*	VF 9	N	10
	Quebracho pH 4.5 H ₃ PO ₄ 1/4 g/l	1—3	10	N	10
	Quebracho pH 4.5 H ₃ PO ₄ 1/2 g/l	1—1	10	N	10
	Quebracho pH 4.5 H ₃ PO ₄ 1 g/l	0—1	10	N	10

This experiment indicates that the concentration of the tannin containing post-treatment can be varied and still obtain improved corrosion and humidity resistance of conversion coated metal surface.

Panels were dried and painted with an automotive body system as in Example 1. The humidity and salt spray resistance of the panels are shown below.

EXAMPLE 4

Cold rolled SAE 1010 steel panels and minimum spangle temper-rolled commercial hot dipped galvanized panels were conversion coated according to the sequence outlined in Example 1. As post-treatments were used a 1 gram per liter solution of quebracho extract, and a 1 gram per liter solution of a quebracho extract material sulfited to improve its water solubility in the concentrated state, both of the above adjusted to a pH of 4.5 with hydrofluoric acid. In addition, another post-treatment consisted of a 1/2 gram per liter quebracho extract solution adjusted to a pH of 4.5 with hydrofluoric acid, and a 1/4 gram per liter solution of a quebracho extract adjusted to a pH of 4.5 with hydrofluoric acid to which was added 0.01 grams per liter aluminum fluoride.

TABLE 4

	Rinse	Salt Spray	Humidity G	
55	Bisulfited Quebracho—CRS	4—6	10	80
	Bisulfited Quebracho—GALV.	0—1	10	
60	Quebracho—CRS	1—3	10	
	Quebracho—GALV.	N	10	
	Quebracho—1/4 g/l pH 4.5 HF—CRS	0—2	10	85
	Quebracho—1/4 g/l pH 4.5 HF—GALV.	0—2	M9	
65	Quebracho—1/4 g/l plus AlF ₃ pH 4.5 HF—CRS	0—2	10	90
	Quebracho—1/4 g/l plus AlF ₃ pH 4.5 HF—GALV.	0—1	10	

These results show that sulfiting the quebracho extract degrades the corrosion resistance of conversion coated and painted CRS but not GALV. surfaces that had been post-treated with a composition produced therefrom, when compared to the same extract non-sulfited, without harming the humidity resistance thereof. Absence of aluminum fluoride had no effect on either corrosion on humidity resistance, on the other hand.

EXAMPLE 5

SAE 1010 cold rolled mild steel and mini-

mum spangle temper rolled commercial hot dip galvanized steel panels were conversion coated as described in Example 1 and subjected to post-treatment with a tannin composition consisting of 1 gram per liter of quebracho extract, the pH of which was adjusted downward with hydrofluoric acid. The panels were then painted with the automotive body system described in Example 4 and the humidity and salt spray resistance of the said panel tested as in Example 1. The results of these tests are shown in Table 5.

TABLE 5

	pH	Metal	336 Hours Salt Spray	336 Hours Humidity
30	7.8	CRS	3—5	10
	7.8	GALV.	0—1	FM9
	7.5	CRS	3—6	10
	7.5	GALV.	0—1	FM9
	5.5	CRS	2—3	VF9
	5.5	GALV.	0—1	10
35	4.5	CRS	0—2	10
	4.5	GALV.	0—2	M9
	3.7	CRS	0—3	10
	3.7	GALV.	0—1	10
40	Control— Chrome	CRS	0—1	VF 9.5

EXAMPLE 5-A

Following the procedure of Example 5, a tannin composition consisting of 1 g/l of tannic acid (NF powder grade from Penick) was adjusted to a pH of 4.0. The adjusting acids were hydrofluoric acid, phosphoric acid and

acetic acid. The panels were then painted with the automotive body system described in Example 1 and the humidity and salt spray resistance of the said panels tested are shown in Table 5-A.

TABLE 5-A

	pH	Metal	336 Hours Salt Spray	336 Hours Humidity
55	H ₃ PO ₄	CRS	0—1	10
	H ₃ PO ₄	GALV.	1—1	M9
	HF	CRS	1—2	VF9
	HF	GALV.	1—1	FM9
	CH ₃ COOH	CRS	0—2	VF9
	CH ₃ COOH	GALV.	1—3	M9
60	Tap Water	CRS	3—5	M9
	Tap Water	GALV.	1—2	D4

From Tables 5 and 5-A, it can be seen that the composition of the present invention is useful over a broad range of pH conditions, from a pH of 3 to a pH of 8. For the best corrosion resistance, as defined by the aforesaid ASTM B117-61 salt spray test, the pH should preferably be within a narrower range of from 4 to 6.0.

EXAMPLE 6

SAE 1010 cold rolled mild steel and temper rolled minimum spangle commercial hot

dip galvanized steel panels were conversion coated as described in Example 1 and subjected to a post-treatment with a tannin composition consisting of 1 gram per liter solution of quebracho extract adjusted to a pH of 4.5 with phosphoric acid. The temperature of this post-treatment solution was varied from 85°F. to 145°F. The panels were then dried, painted as in Example 1 and tested in salt spray and humidity as described in Example 1. The results of this testing are shown in Table 6.

TABLE 6

	Spray Time Seconds	Bath Temperature	Metal	336 Hours Salt Spray	336 Hours Humidity
5	15	85°F.	CRS	1—2	10
	15	85°F.	GALV.	N	10
	30	85°F.	CRS	2—3	VF9
	30	85°F.	GALV.	0—1	10
	60	85°F.	CRS	1—3	10
10	60	85°F.	GALV.	0—1	10
	120	85°F.	CRS	2—3	10
	120	85°F.	GALV.	0—1	10
	30	104°F.	CRS	2—3	10
	30	104°F.	GALV.	N	10
15	30	120°F.	CRS	0—1	10
	30	120°F.	GALV.	0—1	10
	30	140°F.	CRS	2—4	10
	30	140°F.	GALV.	N	10
	30	160°F.	CRS	3—4	10
	30	160°F.	GALV.	0—1	10

20 These results indicate the usefulness of the composition of this invention over a broad range of temperatures.

EXAMPLE 7

25 A tannin composition was made by dissolving 250 grams of quebracho extract in 750 grams of water and adjusting the 25% quebracho solution to a pH of 8 with sodium hydroxide in order to put most or all of the quebracho into solution. A post-treatment

composition was made from the said 25% concentrated quebracho solution by dissolving four grams of the said solution per liter of water. The pH of this post-treatment solution was then adjusted to 4.5 with phosphoric acid. Panels were processed as described in Example 1, post-treated in the said post-treating solution, dried and painted with the automotive body system as in Example 1, and corrosion and humidity tested as described in Example 1. The results of this testing are shown in Table 7.

TABLE 7

	Rinse	Metal	Salt Spray	Humidity
45	No NaOH used in preparation	CRS	0—1	10
	No NaOH used in preparation	GALV.	1—1	VF9
	pH of quebracho concentrate at 8.0	CRS	0—1	10
	pH of quebracho concentrate at 8.0	GALV.	1—1	10

50 These results show that the utility of the presently described post-treatment is not harmed by the manufacture of a concentrated material using an alkali metal hydroxide to adjust the pH in order to solubilize the

quebracho therein contained. Such a concentrate has the advantages of being easy to ship and convenient to use to replenish a producing processing tank by pumping the solution to the tank as required.

EXAMPLE 8

60 Panels were conversion coated as in Example 1 and rinsed in several tannin post-treating compositions, all at a concentration of 1 gram per liter of the tannin extract and all adjusted to a pH of 4.5 with phosphoric acid. Included were technical grade tannic

acid, purified tannic acid, and quebracho extract. The said panels were then oven dried as described in Example 1, painted with an automotive body paint system as described in Example 1 and corrosion and humidity tested as described in Example 1.

TABLE 8

	Aromatic Alkyl Ratio	Metal	336 Hours Salt Spray	336 Hours Humidity
75	1.5/1—Technical Tannic Acid	CRS	7—9	10
	1.5/1—Technical Tannic Acid	GALV.	0—1	10
	3.8/1—NF Grade Tannic Acid	CRS	0—1	10
	3.8/1—NF Grade Tannic Acid	GALV.	N	10
	4.5/1—Quebracho Extract	CRS	1—3	10
80	4.5/1—Quebracho Extract	GALV.	N	10

The results show that the purity of the tannin used is important particularly to the corrosion resistance of the conversion coated, post-treated and painted metal ware.

EXAMPLE 9

SAE 1010 cold rolled steel panels were conversion coated as described in Example 1 with the exception that the conversion coating solution consisting of an aqueous alkali metal phosphate solution as described in U.S. Patent No. 2,609,308 which contains sodium dihydrogen phosphate and sodium chlorate and upon analysis was found to contain 1% by weight PO_4 and 0.5% by weight ClO_3 , and to have 10 total acid points—measured by titrating a 10 ml sample of the solution against 0.1N sulfuric acid to a pink end point using phenolphthalein as indicator—and a pH of 5.3. A tannin composition solution was mixed containing 1 gram per liter of quebracho extract, adjusted to a pH of 4.5

with H_3PO_4 and was used for post-treating the above panels. Additional panels were dipped for thirty seconds into an aqueous chromium containing post-treatment containing 0.05% by weight CrO_3 and having a pH of 3.4. Further panels were tested that had no post-treatment. These panels were oven dried as described in Example 1 and painted with an automotive under body primer. The panels were then corrosion and humidity tested as described in Example 1. The humidity rating in this table is shown in two columns. The G ratings represent the general blistering as described in Example 1 and the A ratings represent the blistering at a portion of the bottom of the panel where a "bead" of post-treatment solution is allowed to form during drying thus concentrating the post-treatment chemical. The latter represents a pocket of post-treatment solution such as might accumulate in a poorly drained area of the work on a production line. The results are shown in Table 9.

TABLE 9

Rinse	336 Hours Salt Spray	336 Hours Humidity Ratings	
		A	G
Control Chrome	0—2	D9	10
Tap Water	3—6 ⁹⁸	D9	10
Deionized Water	3—7 ¹⁰⁸	10	10
Quebracho 1/2 g/l—pH 4.5	2—3	10	10

These results show the utility of the present invention with the so-called iron phosphate conversion coatings, of which the above is an example. They also show one superiority of the present invention in preventing undesirable humidity blistering in the most critical areas, as shown by the A ratings.

EXAMPLE 10

SAE 1010 cold rolled steel panels and temper rolled minimum spangle commercial hot dip galvanized steel panels were conversion coated on an automotive body pre-treatment line by attaching the panels to automobile bodies being treated therein. The treatment consisted of a minute exposure to a spray cleaner as described in Example 1, a warm water rinse for one minute, conversion coating by a minute exposure to a zinc phosphating solution as also described in Example 1, a water rinse for one half minute, exposure to a tannin composition spray consisting of 0.6

gm. the quebracho containing concentrate as described in Example 7 per litre of water and adjusted to a pH of 4.2 with the phosphoric acid. This post-treatment was followed by a short exposure to a spray of a solution mixed from the same concentrate at 0.3 gm. per litre of water. These compositions were automatically maintained by pumping the concentrate and phosphoric acid at the appropriate rates. For comparison, similar panels had been run at an earlier time in the same production line with the post-treatment being one which contained 0.04% by weight chromic acid at a pH of 4, with a .01% by weight chromic acid at the same pH in the final tank. These panels were dried in the oven on the production line. They were painted with an automotive body paint system consisting of a primer, primer-surface, and top coat and exposed to the salt spray test described in Example 1. The results of 336 hours exposure are shown in Table 10.

TABLE 10

	Metal	Post-Treatment	Salt Spray
	Steel	Chromic Acid	0—1
	Galvanized	Chromic Acid	N
5	Steel	quebracho Extract	0—1 ^{3a}
	Galvanized	"	0—1 ^a
	Steel	"	0—1 ^{2a}
	Galvanized	"	0—1
	Steel	"	0—1
10	Galvanized	"	0—1 ^a

These results show the utility on the production line of the concentrated composition described in Example 7.

WHAT WE CLAIM IS:—

- 15 1. A method for coating a metallic surface comprising coating the surface with a conversion coating composition containing iron or zinc and phosphate ions and subsequently coating the thus-coated surface with a tannin-containing composition.
- 20 2. A method according to claim 1 in which the tannin is an extract of a naturally occurring tannin.
- 25 3. A method according to claim 2 in which the extract is of Chinese gall, myrobalan, divi-divi, valonia, sumac, chinchona, mangrove, wattle, eucalyptus, cutch, quebracho, hemlock, mimosa, oak or gambier.
- 30 4. A method according to claim 2 in which the tannin is a hydrolysable tannin.
5. A method according to claim 2 in which the tannin is a condensed tannin.
6. A method according to any preceding claim in which the tannin is a non-sulphite tannin extract.
- 35 7. A method according to claim 1 in which the tannin is tannic acid.
8. A method according to claim 1 in which the tannin is a quebracho extract.

9. A method according to any preceding claim in which the tannin is present in the tannin-containing composition in an amount of less than 1% by weight.

10. A method according to any preceding claim in which the tannin is present in the tannin-containing composition in an amount from 0.1 to 10 grams per litre.

11. A method according to any preceding claim in which the pH of the tannin-containing composition is from 3 to 8.

12. A method according to claim 11 in which the pH is from 4 to 6.

13. A method according to claim 12 in which the tannin-containing composition contains phosphoric acid.

14. A method according to claim 1 substantially as hereinbefore described with reference to any of the Examples.

15. A metal article having a surface coated by a method according to any preceding claim.

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TABLE 10

	Metal	Post-Treatment	Salt Spray
	Steel	Chromic Acid	0—1
	Galvanized	Chromic Acid	N
5	Steel	quebracho Extract	0—1 ^{3a}
	Galvanized	"	0—1 ^a
	Steel	"	0—1 ^{2a}
	Galvanized	"	0—1
	Steel	"	0—1
10	Galvanized	"	0—1 ^a

These results show the utility on the production line of the concentrated composition described in Example 7.

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- 35 6. A method according to any preceding claim in which the tannin is a non-sulphite tannin extract.
7. A method according to claim 1 in which the tannin is tannic acid.
8. A method according to claim 1 in which the tannin is a quebracho extract.

9. A method according to any preceding claim in which the tannin is present in the tannin-containing composition in an amount of less than 1% by weight.

10. A method according to any preceding claim in which the tannin is present in the tannin-containing composition in an amount from 0.1 to 10 grams per litre.

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15. A metal article having a surface coated by a method according to any preceding claim.

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